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Z.H. Wang, A.J. Epstein, A.Ray and A.G. MacDiarmid

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ELECTRON LOCALIZATION IN POLYANILINE AND ITS DERIVATIVES

Z.H. WANG

Department of Physics, The Ohio State University, Columbus (U.S.A.)

A.J. EPSTEIN

Department of Physics and Department of Chemistry

The Ohio State University, Columbus (U.S.A.)

A. RAY* and A.G. MACDIARMID

Department of Chemistry, University of Pennsylvania, Philadelphia (U.S.A.)

ABSTRACT

Electron localization in HCl salt form of polyaniline (PAN-ES) and its methyl ring-substituted derivative, poly(o-toluidine)(POT-ES), has been investigated by optical, transport and magnetic studies. Compared with PAN-ES, POT-ES has increased electron localization though the band structure, crystallinity and intrachain coherence length are similar for the two polymers. The localization is proposed to be induced by a CH_3 group on each C_6 ring which decreases the interchain diffusion rate through reduction of interchain coherence and increased interchain separation.

INTRODUCTION

The achievement of high conductivity σ for polymers has both theoretical and practical importance. Often high σ has been attributed to increase of conjugation length[1]. Though the decrease of conjugation length does decrease the conductivity[2], other factors may be more important in control of very high conductivity of polymers. It is well-known that in a strictly one-dimensional disordered system (1d-DS) all electron states are localized with any weak disorder[3]. However polymer systems are quasi 1d-DS (q1d-DS) where interchain diffusion is not negligible. The interchain diffusion rate w plays an important role in electron localization of a q1d-DS[4,5]. It can be shown[4,5] that with increase of w the electron localization length α^{-1} and σ of a q1d-DS increase. The value of w depends on interchain transfer integral t_{\perp} , interchain coherence length ξ_{\perp} and intrachain coherence length ξ_{\parallel} [4,5] or conjugation length. Thus the increase of the conjugation length or ξ_{\parallel} does increase α^{-1} and σ of polymers. However the other two factors may also play important roles in electron localization. We explore their importance in this paper.

*Present address, Alchemi Research Center, Thane-400601, Maharashtra, India

PAN and POT were synthesized in the base and salt form as described earlier[5](Fig.1a). Pressed pellets were used for most of the transport measurements, with the exception of microwave studies where films cast from N-Methyl-2-Pyrrolidinone were used. A four-probe technique was utilized for σ_{dc} measurements. The 'cavity perturbation' technique was adopted for the microwave measurement. EPR X-band measurements utilized a Bruker EPS 300 spectrometer. The static χ was measured by Faraday technique[5].

The EPR peak-to-peak linewidth (Fig. 1b) of POT-ES monotonically decreases from 2.7 G to 0.7 G as T increases from 4 K to 300 K, however that of PAN-ES has very little T-dependence (~ 0.3 G). The optical absorption spectra of PAN-ES and POT-ES in aqueous 80% acetic acid (inset of Fig. 1b) are qualitatively the same. For both polymers $\sigma \propto \exp[-(T_0/T)^{1/2}]$, but $T_0 = 5000$ K for PAN-ES and 30000 K for POT-ES (Fig. 2a). The room temperature σ of PAN-ES is about $10^0 \sim 10^1$ S/cm, and that of POT-ES is $10^{-3} \sim 10^{-2}$ S/cm, depending on moisture, ageing, doping, etc. The dielectric constants ϵ at frequency 6.5 GHz increases with T, from 20 to 100 for PAN-ES and 7 to 10 for POT-ES as T from 50 K to 300 K. The thermoelectric powers $S(T)$ of the two polymers have similar U-shape T-dependence (inset of Fig. 2b). The minimum of $S(T)$ for PAN-ES is between 150 K and 200 K and for POT-ES it is approximately 300 K. At low T (< 300 K), $S(T)$ of POT-ES can be expressed as $A + B/T$ [5], while $S(T)$ of PAN-ES can be approximately decomposed into $A + B/T + CT$ [7].

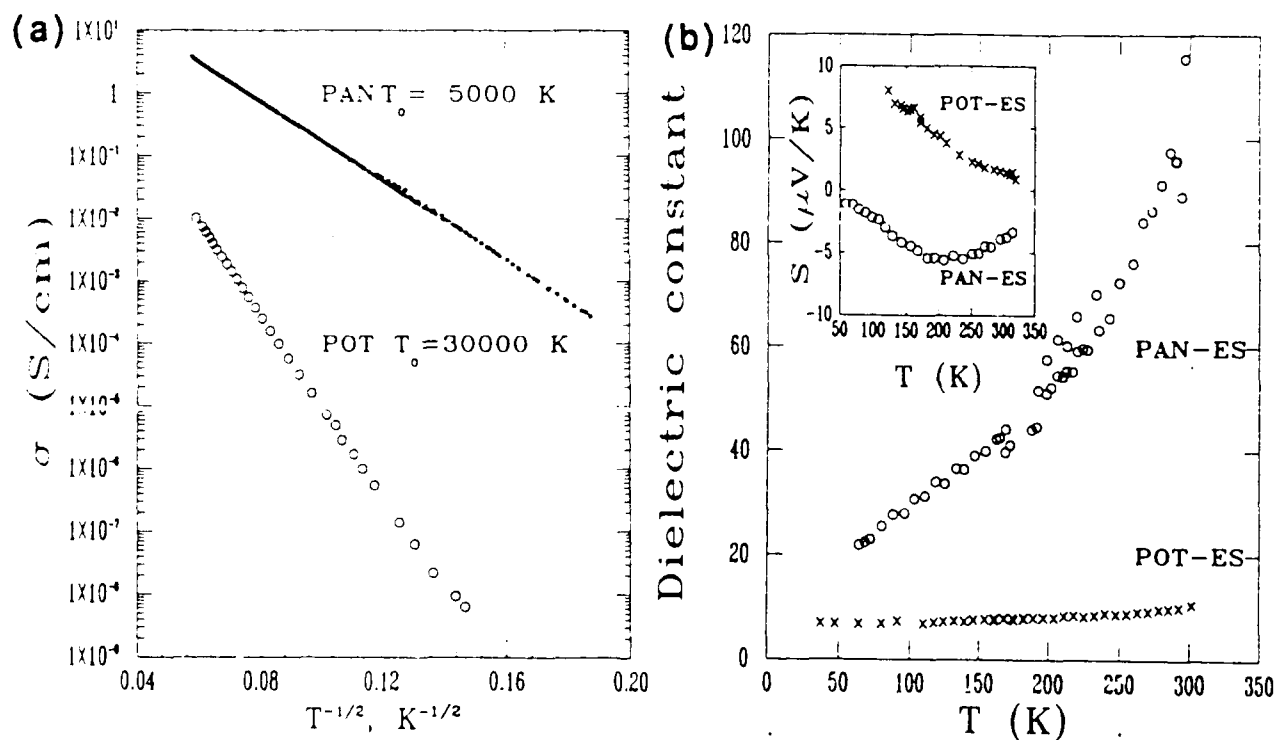


Fig.2 (a) DC conductivity of PAN-ES (●) and POT-ES (○). (b) Dielectric constant of unoriented PAN-ES (○) (Javadi et al, *Phys. Rev. B*, 39 (1989) 3579.) and POT-ES (×). Inset is thermoelectric power of PAN-ES (○) and POT-ES (×).

We compare here two polymers, the HCl salt form of polyaniline (PAN-ES) and its methyl ring-substituted derivative, poly(o-toluidine) (POT-ES) (Fig.1a)[5]. They have similar electronic structures, crystallinity and more importantly $\xi_{||}$, but different ξ_{\perp} and interchain space or t_{\perp} [5,6]. Analyses of T-dependent DC conductivity $\sigma_{dc}(T)$, electric field dependent $\sigma(E)$, thermopower $S(T)$, microwave conductivity and dielectric constant ϵ at 6.5 GHz, susceptibility χ , and electron paramagnetic resonance (EPR) linewidth and lineshape together show that there is greater electron localization in POT-ES as compared with that in PAN-ES[5]. Our study together with the results of X-ray studies[6] suggests that the increased electron localization in POT is associated with the increased one-dimensionality induced by decreased interchain diffusion rate due to (i) the increased interchain separation and (ii) greater interchain disorder within the crystalline regions. Both are due to existence of CH_3 on C_6 rings. The CH_3 has larger size than H and its location at the "a" or "b" position of C_6 ring (Fig.1a) is dependent on ring flipping. Hence it induces an increase of interchain spacing and disorder. The transport data suggest that conduction is due to quasi-1d variable range hopping [5]. Based on this model quantitative analyses show α^{-1} for POT-ES is several Å, while for PAN-ES is a few tens Å.

EXPERIMENTAL TECHNIQUES AND RESULTS

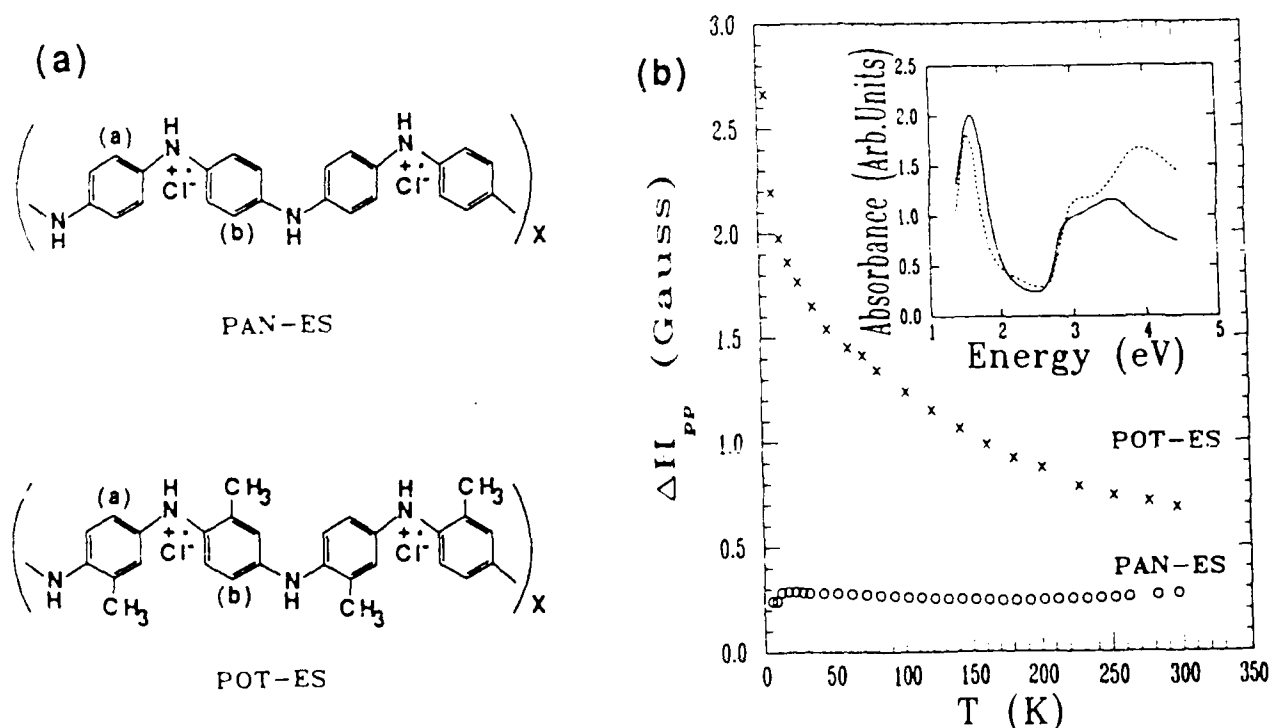


Fig.1 (a) Schematic structure of PAN-ES and POT-ES. (b) EPR peak-to-peak linewidth of PAN-ES (o) (from P. Vaca et al, to be published) and POT-ES (x). Inset is the optical spectra of PAN-ES (solid line) and POT-ES (dashed line) in aqueous 80% acetic acid.

DISCUSSION

The EPR linewidth, DC conductivity, microwave dielectric constant and thermoelectric power altogether reflect increased electron localization in POT-ES compared with PAN-ES. The narrowed EPR linewidth indicates a strong spin motional or exchange narrowing[5]. The greater EPR linewidth as well as lower conductivity and dielectric constant in POT-ES is a signature of increased spin localization in POT-ES[5]. The T-dependence of $\sigma(T) \propto \exp[-(T_0/T)^{1/2}]$ and $S(T) \propto A + B/T$ (at low temperatures) indicating a q1d-VRH of charges between nearest neighboring chains[5]. Within the model, $T_0 = 16\alpha/N(E_F)k_B z$ [5] where $N(E_F)$ is density of states at Fermi energy, k_B is the Boltzmann constant and z is the number of nearest neighboring chains. Utilizing $N(E_F) = 3.5$ (PAN-ES) and 1.7 (POT-ES) states/eV-2rings[5], we obtain $\alpha^{-1} \sim 30 \text{ \AA}$ for PAN-ES and 9 \AA for POT-ES.

Two polymers have very similar electronic structures and crystallinity, but very different electron localization and transport properties. Based on the EPR lineshape analyses[5] and x-ray studies[6], the increased electron localization is attributed to the decreased interchain diffusion rate, associated with the decrease of ξ_{\perp} and increased interchain separation (decrease of t_{\perp}), not with the change in conjugation length. The studies of oriented PAN-ES[7] suggest that PAN-ES represents a new class of q1d disordered conductors where electrons are delocalized to a bundle of chains with the dimension determined by ξ_{\perp} [7] while POT-ES remains as a non-metal. Our results demonstrate that maximizing interchain coherence and transfer integral is essential to improve the conductivity of polymers.

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